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Several addition reactions of ethylenimine with various amino compounds, using water as a catalyst have been reported by Wilson (1).

Substituted diamines have been prepared most commonly by a Gabriel Synthesis (2) from primary and secondary amines and B-bromoethylphthalimide, and through the reaction of ethylene oxide with amines to form ethanolamine from which the diamine could be prepared (3). However, the addition of primary and secondary amines to ethylenimine represents a direct and simple method for their preparation, providing satisfactory yields can be obtained.

In the present work, a study of this addition reaction as catalyzed by aluminum chloride has been made. The use of aluminum chloride has certain advantages over the use of water since the reaction is carried out under anhydrous conditions and in many cases the isolation of products is more easily effected than when a large volume of water is used. So far as the present authors are aware, the catalysis by aluminum chloride of such an addition has not been previously reported.

The general procedure for the addition reaction involved the splitting of the three-membered heterocyclic ring in ethylenimine by a primary or secondary amine in the presence of aluminum chloride in benzene solution.

$$RNH_2 + H_2C\text{—}CH_2 \xrightarrow[C_6H_6]{ALCL_3} R\text{-}N\text{-}C\text{-}C\text{-}NH_2$$

(the ethylenimine ring is NH bridging the two CH$_2$ groups; the product has H H H and H H)

The reactions, which were in general quite exothermic, were con trolled by placing an ice bath around the reaction flask.

The primary and secondary amines used in this study together with the products formed by addition and the yields obtained under the experimental conditions are listed in Table I.

It should benoted that the reactions were carried out at relatively low temperatures and that the ethylenimine was added in liquid form. Further work in this laboratory (4) has indicated that better yields are obtainable at higher reaction temperatures and by a vapor phase addition of the ethylenimine.

TABLE 1

PRODUCTS FORMED FROM ETHYLENIMINE AND PRIMARY AND SECONDARY AMINES

AMINO COMPOUND	PRODUCT FORMED	YIELD
Diethylamine	N'-diethylethylenediamine	51.9%
Dibutylamine	N'-dibutylethylenediamine	46.2%
Dinamylamine	N'-di-n-amylethylenediamine	34.1%
Aniline	N'-phenylethylenediamine	52.0%
MethylAniline	N'N'-methylphanylethylene-diamine	44.8%
Benzylamine	N'-benzylethylene diamine	12.0%

EXPERIMENTAL

Ethylenimine. This compound was prepared from b-aminoethylsulfate* by the method of Wenker (5). In a typical run 282 grams of b-aminoethylsulfate was mixed with 880 grams of 40% caustic soda solution and heated in a three liter flask. The ethylenimine-water mixture that distilled over was separated by treatment with solid potassium hydroxide. The pure ethylenimine distilled at 55-56.5°c., $n_D^{25°}=1.4118$. Average yield was 25%, based on the aminoethylsulfate.

N,N-diethylethylenediamine,[*1] One hundred grams (0.75 mole) of aluminum chloride was suspended in 100 ml. of dry benzene in a 1-liter, 3-necked round bottomed flask equipped with reflux condenser provided with a calcium chloride tube, mechanical stirrer, and a dropping tube also protected by a calcium chloride tube. To this suspension 150 grams (2.05 moles) of diethylamine was added dropwise with stirring. The reaction flask was cooled in an ice bath. This was thought to be necessary due to the heat of the reaction. After the addition of the diethylamine, the mixture was allowed to cool with stirring for 30 minutes. The reaction mixture was a clear, reddish solution. To the cooled solution 21.5 grams (0.5 mole) of ethylenimine was added dropwise with stirring, and the mixture stirred in an ice-bath for two hours after completion of the imine addition.

The isolation of the diamine was effected by the addition of an excess of 40% sodium hydroxide to the reaction mixture, which formed two layers. After separating the benzene layer, the water layer was extracted twice with 50 cc. portions of benzene, and these extractions were added to the original benzene layer. The mixture was dried repeatedly with potassium hydroxide and finally with anhydrous potassium carbonate. The solvent was evaporated and the diamine separated from the unreacted amine and ethylenimine by fractional dis-

* Contributed by Carbide and Carbon Chemical Corp.
[*1] The addition of diethylamine to ethylenimine as catalyzed by aluminum chloride was first carried out by R. L. Sundberg in this laboratory.

tillation. In this particular reaction it was impossible to recover the excess amine in a pure form since its boiling point is the same as that of ethylenimine.

The N,N-diethylethylenediamine was a clear, light yellow liquid boiling at 141-143°C. It was identified further by its index of refraction. Recorded, n_D =1.4360; Found, n_D =1.4356 Yield, 30.2 grams (51.9%).

The reactions of ethylenimine with the other amines listed in Table I, were carried out with only minor variations in procedure.

In Table II are listed the products of these additions, their physical properties and derivatives prepared in certain cases for identification purposes.

TABLE II

PHYSICAL PROPERTIES AND DERIVATIVES OF DIAMINES

DIAMINE	B.P.	n_D	DERIVATIVE	M.P.
$(C_2H_5)_2NCH_2CH_2NH_2$	141-143°	1.4356	.....	.....
$(C_4H_9)_2NCH_2CH_2NH_2$	100°/13mm	.....	a-napthyl urea	101.3°
$(C_5H_{11})_2NCH_2CH_2NH_2$	125°/15mm	.....	.....	.....
$C_6H_5NHCH_2CH_2NH_2$	262-264°	.....	picrate	179-180
$C_6H_5N(CH_3)CH_2CH_2NH_2$	254-255°	.....	picrate	173
$C_6H_5CH_2NHCH_2CH_2NH_2$	162°/20mm	.....	picrate	222(d)

SUMMARY

The addition reaction between primary and secondary, aliphatic and aromatic amines and ethylenimine as catalyzed by aluminum chloride has been studied as a direct method of preparing N-substituted diamines.

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